

Electron spin resonance and magnetization in $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ thin films

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Abstract

We report electron spin resonance (ESR) and magnetization measurements in $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ thin films deposited on LaAlO_3 single-crystal substrates by DC sputtering technique. Angular and temperature dependence of resonance field (H_{Res}) and ESR line-width (ΔH_{PP}) were measured in the ferromagnetic and paramagnetic regime. Above T_C , H_{Res} is not shifted, while below T_C , H_{Res} for H^\perp and H^\parallel diverge, due to the presence of magnetic anisotropy and demagnetizing fields. Besides, when T is approaching T_C from above, the ΔH_{PP} goes to a minimum (≈ 200 G) and ΔH_{PP} increases below T_C . Temperature dependence of magnetization in the films was obtained by using the relationship of H_{Res} . These values were compared with SQUID measurements. Finally, we estimated the gyromagnetic factor in 1.996(6).

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PACS: 76.30.-v; 75.70.-i; 75.47.Lx

Keywords: Electron Spin Resonance; Thin films; Magnetoresistance; Manganites

Lanthanum-based manganites, with the general formula $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ and Perovskite structure, have been extensively studied both for their basic research and possible technological applications, since the discovery of colossal magnetoresistance (CMR) [1]. The electron spin resonance (ESR) technique has played a key role in the study of manganites, because ESR is sensitive to changes in magnetization behavior in the ferromagnetic (FM) and paramagnetic (PM) regime, and transport properties of thin manganite films focused on microwave absorption studies [2–5]. However, only a few studies have been performed on $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ (LCMO) thin films using ESR. In order to analyze the magnetic properties and to estimate the gyromagnetic factor (g) related to the CMR system, we performed ESR and SQUID measurements in LCMO thin film samples.

LCMO thin films were grown on LaAlO_3 single-crystal substrates by DC sputtering technique. The resonance

measurements in FM and PM regime, were performed in the X-band at a fixed frequency (9.58 GHz), using a Bruker spectrometer ESP300E. The sample was rotated in a microwave cavity by using a Bruker goniometer at an arbitrary angle (α) between the external DC magnetic field (H) and the film plane, from 0° to 360° . Angular dependence of the resonance field (H_{Res}) and the resonance peak-to-peak line-width (ΔH_{PP}) were measured at room temperature. As a function of temperature, ΔH_{PP} and H_{RES} were measured between 250 and 400 K, for parallel (H^\parallel) and perpendicular (H^\perp) field orientation in relation to the film plane. Temperature dependence of the magnetic moments was measured using a quantum design SQUID magnetometer in an external field of 300 and 3480 G.

The ESR spectra obtained at room temperature in the PM regime at different angles α consists of a single symmetric line well-resolved for the LCMO films with Lorentzian shaped lines. The symmetric ESR signal with Lorentzian line shape is maintained on angular variation. This behavior can be regarded as good film quality. For this line shape, ΔH_{PP} , H_{Res} and g -factor were derived by

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fitting to the experimental data. Fig. 1 shows $H_{\text{Res}}(\beta)$ at room temperature, where $\beta = \alpha - 214.4(3)^\circ$, and represents the correct angle between H and the film plane. The initial angle $214.4(3)^\circ$ was obtained from the ESR line fit. The inset shows that the $\Delta H_{\text{PP}}(\beta)$ of the resonance, for β equals to 0° and $\pm 90^\circ$, goes to a minimum for H^{\parallel} (~ 217 G) and maximum for H^{\perp} (~ 231 G). Our results are in concordance with those presented by Ivanshin, et al. [6], who show the angular dependence of ΔH_{PP} in the PM regime in $\text{La}_{0.95}\text{Ca}_{0.05}\text{MnO}_3$ single crystals. They found that ESR behavior is very dependent on the sample, attributed to the magnetic inhomogeneity of the samples, in the AF and FM phases, given local variations of oxygen stoichiometry and the chemical composition. Probably, this behavior can be also present in our manganite thin film measurements. Additionally, from the experimental data above, we have made the estimation of the g -factor, by carrying out

algebraic manipulations and approximations to Kittel equations for H_{Res} in samples with plane geometry [7], and taking into account the demagnetizing factor for this geometry, we can derive the following expression for H_{Res} :

$$H_{\text{R}} = H_{\text{LCMO}}^{\text{Res}} - 2\pi M(1 - 3\sin^2(\beta)), \quad (1)$$

where $H_{\text{LCMO}}^{\text{Res}}$ is the resonance field for the LCMO films, M is magnetization and β is the resonance angle. From the fit, we found $H_{\text{Res}} = H_{\text{LCMO}}^{\text{Res}}$ when $\beta = 35.26(4)^\circ$. This leads to $H_{\text{LCMO}}^{\text{Res}} = 3496.8(1)$ G (see Fig. 1), and using the expression $g_{\text{LCMO}} = g_{\text{DPPH}} H_{\text{O}}^{\text{DPPH}} / H_{\text{LCMO}}^{\text{Res}}$, where $g_{\text{DPPH}} = 2.0038$, $H_{\text{O}}^{\text{DPPH}} = 3484.2$ G resonance field of DPPH, we obtained the g -factor for LCMO films that corresponds to $1.996(6)$, coinciding with the g -factor value ranges reported by studying manganites at X and Q band frequencies [2–4].

The ESR spectra, as a function of temperature taken in H^{\parallel} and H^{\perp} , are shown in Fig. 2. Observe that the ESR spectra have an asymmetric line shape, both ferromagnetic resonance and EPR, above and below the magnetic transition ($T_{\text{C}} \sim 275$ K), but the spectra do not show a typical behavior of spin wave resonance (SWR) in contrast to ESR studies in thin films of other manganites such as $\text{La}_{0.7}\text{X}_{0.3}\text{MnO}_3$, where $\text{X} = \text{Ba}, \text{Sr}$ [5,8,9]. In spite of the same Mn^{3+} and Mn^{4+} proportion, mentioned in the above studies, we still do not know why SWR does not appear in LCMO thin films. At the same time, in Fig. 2, both intense and broad signals, with large variation, both in line intensity and in ΔH_{PP} when temperature is lowered through T_{C} , are observed. As T approaches minimum at $T_{\text{min}} \approx 1.04T_{\text{C}}$ from above, the ΔH_{PP} was found to be almost linear with T , going through a minimum (~ 200 G) and then increasing rapidly below T_{min} . Also, the increase of ΔH_{PP} below T_{min} is an effect observed in single crystal manganites and other magnetic materials that do not show CMR [3,10,11]. As a function of the temperature, in Fig. 3, H_{Res} are shown in both H^{\parallel} and H^{\perp} . Observe that above the T_{min} in both configurations, resonance field remains at its paramagnetic limit (~ 3400 G). Below T_{min} , the field

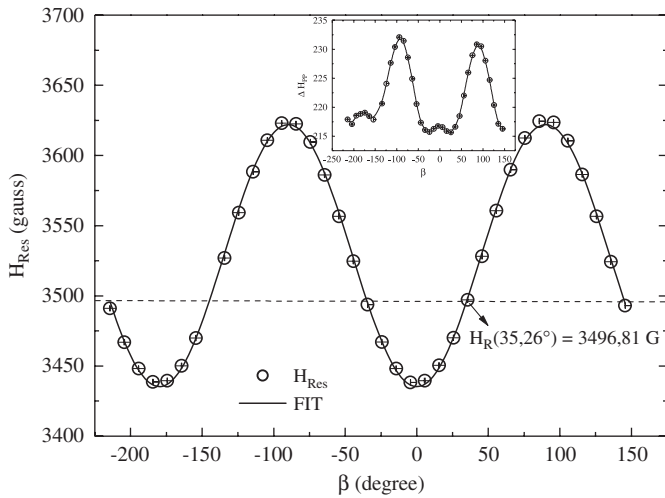


Fig. 1. $H_{\text{Res}}(\beta)$ at room temperature, the continuous line is the fit by using Eq. (1). Inset shows $\Delta H_{\text{PP}}(\beta)$ for the PM regime. Error bars have the same size that the symbol.

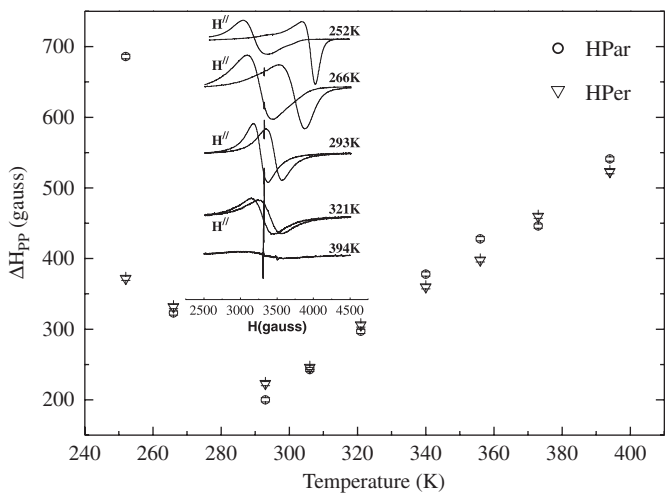


Fig. 2. $\Delta H_{\text{PP}}(T)$ vs. T for LCMO film. Inset shows ESR spectra, as a function of temperature taken in H^{\parallel} and H^{\perp} to the film plane.

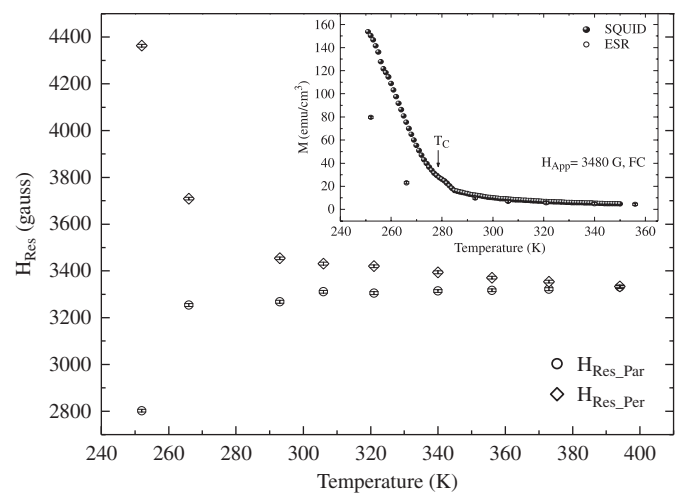


Fig. 3. $H_{\text{Res}}(T)$ vs. T in LCMO film. Inset shows a plot of the DC (fill circles) and ESR (open circles) magnetization.

resonance for H^\perp diverges upward while in H^\parallel it diverges downward, owing to the presence of demagnetizing field and magnetic anisotropy. Similar results in ESR studies in manganite films have been reported [12]. Finally, magnetization was estimated from the H_{Res} field measurements by using the resonance equations of Kittel according to Landau–Lifshitz [7]:

$$\omega = \gamma [H_{\text{R}}^\parallel (H_{\text{R}}^\parallel + 4\pi M)]^{1/2}, \quad (2)$$

$$\omega = \gamma [H_{\text{R}}^\perp - 4\pi M], \quad (3)$$

where $\omega/2\pi = 9.58$ GHz, $\gamma = g\mu_{\text{B}}/\hbar$ is the gyromagnetic ratio, g corresponds to the gyromagnetic factor, and H_{R}^\parallel and H_{R}^\perp are the experimental values of the H_{Res} in H^\parallel and H^\perp geometry, respectively. By making a binomial expansion of Eq. (2) and taking into account that the term $4\pi M/H^\parallel \ll 1$, Eq. (2) is reduced to the following expression: $\omega = \gamma(H^\parallel + 2\pi M)$. Upon subtracting the above expression from Eq. (3), we obtain the following expression for the calculus of the magnetization from resonance measurements: $H_{\text{R}}^\perp - H_{\text{R}}^\parallel = 6\pi M$. The inset in Fig. 3 shows the magnetization M_{ESR} and M_{DC} calculated by the resonance field from ESR and SQUID measurements, respectively. The coincidence of M_{ESR} and M_{DC} in the PM regime studied agrees with the one obtained from measurements for DC and ESR susceptibility in ceramics samples of LCMO, showing that all manganese spins contribute to the observed ESR line [2]. Divergent behavior for M_{ESR} and M_{DC} near T_{C} was observed, probably due to the presence of demagnetizing field and magnetic anisotropy.

In summary, we used ESR measurements to calculate the g -factor for LCMO films (1.996(6)).

Magnetization estimated from H_{Res} , shows divergent behavior close to T_{C} , coinciding with M_{DC} , probably due to the presence of demagnetizing field and magnetic anisotropy. Also, a similar result was obtained below the T_{min} , where the field resonance for H^\perp diverges upward while for H^\parallel diverges downward. Finally, we did not observe spin waves resonance in LCMO thin films, probably due to: changes in crystalline field, order and disorder in ferromagnetic regime caused by substitution in divalent ions, substrate effects, inhomogeneities.

This work has been partially supported by the Excellence Center for Novel Materials under Contract no 0043-2005 with COLCIENCIAS. Colombia. One of the authors, O.A. wishes to thank the support by COLCIENCIAS through fellowship doctoral programme and the Hospitality at the *Laboratoire de Physique du Solide*, Paris, France.

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